

Alameda County Water District
Water Quality Laboratory
ELAP Certificate No. 1524

Quality Assurance Program

STANDARD OPERATING PROCEDURE

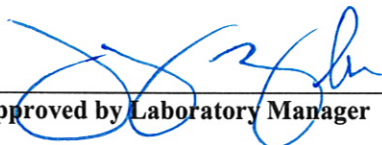
Anions by Ion Chromatography, EPA 300.1
Version #: 1



Reviewed by QA/QC Officer

6/26/2012

Date



Approved by Laboratory Manager

6.26.2012

Date

ALAMEDA COUNTY WATER DISTRICT
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NUMBER
WQL027

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**SUBJECT: EPA 300.1 Determination of Inorganic Anions in
Drinking Water by Ion Chromatography (Part A.).**

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1. Scope and Application

1.1 This SOP is intended for general guidance and defines method specific operating conditions. Additional training with an experienced operator is required. This method covers the determination of the following anions:

Bromide (Br)
Chloride (Cl)
Fluoride (F)
Nitrate as NO₃ (NO₃)
Nitrite as Nitrogen (NO₂-N)
Phosphate as PO₄ (PO₄)
Sulfate (SO₄)

1.2 Ion chromatography (IC) procedure provides an accurate and a rapid measurement for the seven anions listed above.

1.3 The detection limits (DLR) for this procedure are listed in Table 1.

Table 1

Compound	Concentration (mg/L)
Bromide	0.100
Chloride	0.100
Fluoride	0.100
Nitrate as Nitrate	0.100
Nitrite as Nitrogen	0.100
Phosphate as Phosphate	0.100
Sulfate	0.100

2. Safety

2.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for extremely hazardous materials or procedures.

2.2. The following chemicals have the potential to be highly toxic or hazardous. An MSDS should be consulted prior to handling.

2.2.1. Sulfuric Acid (H₂SO₄). (CAS 7664-93-9).

2.2.2. Dichloroacetate (DCA). (CAS 19559-59-2)

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<p>3. Apparatus and Materials</p> <p>3.1. Ion Chromatograph – Metrohm 881 IC Compact Pro system. System includes:</p> <p>3.1.1. Metrohm 858 Professional Sample Processor.</p> <p>3.1.2. Metrohm inline ultrafiltration which filters samples and standards down to 0.2 µm.</p> <p>3.1.3. Metrohm 800 Dosino for inline eluent generation.</p> <p>3.1.4. Metrohm A Supp 7 analytical column (Cat. #6-1006-630)</p> <p>3.1.5. Metrohm Suppressor Module (MSM) with chemical suppression.</p> <p>3.1.6. 20 uL sample loop (Cat. #6.1825.210).</p> <p>3.1.7. 800 Dosino for automatic dilution.</p> <p>3.1.8. MagIC Net 2.2 software.</p> <p>3.2. Sample bottles, 500 mL plastic.</p> <p>3.3. Analytical Balance. ± 0.1 mg sensitivity.</p> <p>3.4. Sample Vials. Metrohm, 11 mL (Cat. #M-2743-120).</p> <p>3.5. Ultrasonic Cleaner.</p> <p>3.6. 10-mL pipettor (Disposable pipettes may be substituted).</p> <p>4. Reagents</p> <p>4.1. Reagent Water: All references to water in this method will refer to organic-free water produced by a Barnstead unit with a resistivity of no less than 18.0 MΩ-cm.</p> <p>4.2. Eluent stock: 72 mM sodium carbonate.</p> <p>4.2.1 Dissolve 7.63 g of sodium carbonate powder in approximately 500 mL of water, QSL with water.</p> <p>4.2.2 Use the eluent generator to prepare the 3.6 mM working eluent.</p>		

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4.3. Anion stock standards. Stock standards are purchased already prepared, but may also be made from salts.

4.3.1. Bromide – 1000 mL, Ultra Scientific (Cat. #ICC-001) or equivalent.

4.3.2. Chloride - 1000 mL, Ultra Scientific (Cat. #ICC-002-5) or equivalent.

4.3.3. Fluoride - 1000 mL, Ultra Scientific (Cat. #ICC-003) or equivalent.

4.3.4. Nitrate as NO₃ - 1000 mL, Ultra Scientific (Cat. #ICC-004) or equivalent.

4.3.5. Nitrite as N - Ultra Scientific (Cat. #ICC-007A) or equivalent.

4.3.6. Phosphate as PO₄ - 1000 mL, Ultra Scientific (Cat. #ICC-005) or equivalent.

4.3.7. Sulfate – 1000 mL, Ultra Scientific (Cat. #ICC-006-5) or equivalent.

4.4. Suppressor rinse: Fill reservoir with reagent water.

4.5. Suppressor regenerant: 0.3 M sulfuric acid.

4.5.1. Dilute 8 mL of concentrated sulfuric acid to 1L with water.

4.6. Surrogate Solution: Dichloroacetate (DCA), Inorganic Ventures, 500 mg/L (Cat. #ICDCA-S-1).

5. Sample Collection, Preservative and Storage

5.1. Samples should be collected in 500 mL amber plastic bottles. All bottles must be cleaned and rinsed with de-ionized water prior to use.

5.2. Sample holding times and required preservatives are summarized in Table 2.

Table 2

Analyte	Preservative	Holding Time
Bromide	None	28 days
Chloride	None	28 days
Fluoride	None	28 days
Nitrate as NO ₃	Cool to 4 °C	48 hours
Nitrite as N	Cool to 4 °C	48 hours
Phosphate as PO ₄	Cool to 4 °C	48 hours
Sulfate	Cool to 4 °C	28 days

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5.3. Degradation of ortho-phosphate has been observed in samples held at room temperature for over 16 hours. Therefore, samples to be analyzed for ortho-phosphate must not be held at room temperature for more than 12 cumulative hours.

6. Calibration

6.1. Prepare an intermediate standard at the concentrations listed in Table 3.

Table 3

Analyte	Concentration (mg/L)
Bromide	10.0
Chloride	10.0
Fluoride	10.0
Nitrate as NO ₃	10.0
Sulfate	10.0

6.1.1. To prepare the intermediate standard, add 5.0 mL of 1000 mg/L stock standard, of each of the analytes listed in Table 3, to a 500-mL volumetric flask. Bring to volume with water. This standard is valid for one month from the preparation date. (This process may also be done gravimetrically.)

6.1.2. Nitrite-N and phosphate must be added fresh daily and are therefore not included in the intermediate standard.

6.2. Prepare six calibration standards to match the concentrations listed in Table 4.

Table 4

Analyte	Std. 1 (mg/L)	Std. 2 (mg/L)	Std. 3 (mg/L)	Std. 4 (mg/L)	Std. 5 (mg/L)	Std. 6 (mg/L)
Bromide	0.1000	0.2000	0.5000	1.000	2.000	5.000
Chloride	0.1000	0.2000	0.5000	1.000	2.000	5.000
Fluoride	0.1000	0.2000	0.5000	1.000	2.000	5.000
Nitrate as NO ₃	0.1000	0.2000	0.5000	1.000	2.000	5.000
Nitrite as N	0.1000	0.2000	0.5000	1.000	2.000	5.000
Phosphate as PO ₄	0.1000	0.2000	0.5000	1.000	2.000	5.000
Sulfate	0.1000	0.2000	0.5000	1.000	2.000	5.000

6.2.1. To prepare the calibration standards listed in Table 4, add the volumes of standard, listed in Table 5, to a 100-mL volumetric flask and bring to volume with reagent water.

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Table 5

Analyte	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6
Intermediate Standard	1.0 mL	2.0 mL	5.0 mL	10 mL	20 mL	50 mL
Nitrite as N (1000 ug/mL)	10.0 µL	20.0 µL	50.0 µL	100 µL	200 µL	500 µL
Phosphate as PO ₄ (1000 ug/mL)	10.0 µL	20.0 µL	50.0 µL	100 µL	200 µL	500 µL

6.2.2. Once prepared, transfer 10.0 mL of standard to a test tube containing 20 µL of 500 mg/L DCA. This will yield a 1.0 mg/L surrogate concentration.

7. Procedure

7.1. Set the IC general operating conditions to match those listed in Table 6.

Table 6

Parameter	Setting
Column	Metrohm A Supp 7 250x4 mm
Guard Column	Metrohm RP2 disk and filter
Column Heater	45 °C
Suppressor (MSM)	Metrohm Chemical
Eluent Flow	0.7 mL/min.
Run Time	32 min.
MSM Rinse	Reagent Water
MSM Regenerate	0.3 M Sulfuric Acid
Eluent	3.6 mM sodium carbonate
Sample Loop	20 µL
Approximate Background Pressure	0.9 psi
Approximate Background Cond.	0.7-1.0 µS

7.2. Place the samples on the bench and allow them to come to room temperature before analysis.

7.3. Turn the IC on and allow the column heater to come up to temperature.

7.4. Once the column is up to temperature, start the IC hardware and let the system stabilize for about 30 minutes. Set the suppressor to automatically step so that all channels are conditioned prior to use.

7.5. Create a sequence table in "Workplace" on the "Determination Series" tab, and print it out. An example sequence is shown in Appendix 1.

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- 7.6. Run two laboratory reagent blanks, the Laboratory Fortified Blank (LFB), which is also used as the Instrument Calibration Check (ICC) and a LFB duplicate. Evaluate these QC samples and proceed with running samples only after these QC samples have met all acceptable QC criteria summarized in Table 7.
- 7.7. Run the sequence. Please note that the sequence may be edited even after the analysis has begun. Therefore, samples may be added on to the end of a run or the order that samples are run may be altered as the run progresses. If there are any changes to the sequence table during the run, the sequence table must be resaved and reprinted at the end. An example of an acceptable sequence table can be found in Appendix I.
- 7.8. Critically evaluate all chromatograms in "Database" and determine if any require manual integration or further dilution. Manual integration should be avoided if at all possible. If manual integration is used, both the before and after chromatograms should be included in the data package along with a memo stating that the chromatogram was manually integrated.
- 7.9. Print out all chromatograms and compile the data package for QC review.

8. Quality Control

- 8.1. Analysis Batch. Analyze no more than 20 field samples (Field samples include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all laboratory fortified sample matrices.) The analysis batch must include an initial calibration check standard, an end calibration check standard, laboratory reagent blank and a laboratory fortified blank. Within an analysis batch, for every group of ten field samples, at least one Laboratory Fortified Matrix (LFM) and either a field duplicate, a laboratory duplicate or a duplicate of the LFM must be analyzed. When more than ten field samples are analyzed, a continuing calibration check standard must be analyzed after the tenth field sample analysis.
- 8.2. Method Detection Limit (MDL). The MDL must be established for all analytes using reagent water fortified at a concentration of 2 to 3 times the estimated instrument detection limit. Use an average of seven replicates (analyzed over a minimum of three separate days) to determine the MDL. A new MDL must be determined:
- 8.2.1. Every 6 months.
 - 8.2.2. When a new operator begins work.
 - 8.2.3. Whenever there is a significant change in the background or instrument response.

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8.3. Peak Gaussian Factor (PGF). The PGF is calculated by the MagIC Net software and appears on all chromatograms. However, the PGF for the ICC is the one that will be reported for the batch. The formula to calculate this manually is as follows:

$$PGF = \frac{1.83 \times W_{(1/2)}}{W_{(1/10)}}$$

Where: $W_{(1/2)}$ is the peak width at one half peak height.
 $W_{(1/10)}$ is the peak width at one tenth peak height.

Acceptable results for PGF are between 0.80 and 1.15.

8.4. Laboratory Reagent Blank (LRB). The LRB must be analyzed before analyzing any samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination. Corrective actions must be taken before continuing the analysis.

8.5. Laboratory Fortified Sample Matrix (LFM). Add a known amount of the analyte to 10% of field samples. The analyte concentration must be high enough to be detected above the original sample. The LFM concentration should not be less than the native amount found in the field sample being spiked or higher than five times the highest concentration found in any field sample in the batch. If no analyte is observed in any field sample, the LFM must be fortified no greater than five times the lowest calibration level.

8.6. Duplicate samples (field or laboratory) should be run on 10% of field samples, or at least one with each batch of samples, whichever is greater. If none of the samples within the batch have measurable concentrations, the LFM should be employed as the laboratory duplicate.

8.7. Surrogate recoveries must be between 90-115%. The calculation is as follows:

$$R = \frac{SRC}{SFC} \times 100$$

Where, R = Percent Recovery
 SRC = Surrogate Recovered Concentration
 SFC = Surrogate Fortified Concentration

8.8. Surrogate retention times must be monitored and cannot shift by more than 5% from the previous run or by 20% from the original recorded retention time.

8.9. The laboratory is required to maintain a historic record of retention times for the surrogate and all target anions to provide evidence of an analytical column's vitality.

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8.10. Quality control acceptance criteria are summarized in Table 7.

Table 7

Quality Control Parameter	Acceptance Range
Calibration Curve	Coefficient of Variance ≥ 0.995 and Relative Standard Deviation $\leq 10\%$
Laboratory Blank (LRB)	All Analytes Below the MDL.
Laboratory Fortified Blank (LFB)	85-115%
Initial Calibration Check Standard (ICC)	85-115%
Continuing Calibration Check Standard (CCC)	85-115%
End Calibration Check Standard (ECC)	85-115%
Laboratory Fortified Sample Matrix (LFM)	75-125%
Peak Gaussian Factor (PGF)	0.80-1.15
Surrogate Recovery	90-115%
Surrogate Retention Time	2% shift with new eluent
Surrogate Retention Time	5% Shift From Previous Run 20% Shift From Original Retention Times
Laboratory Duplicate Analysis (LD1 & LD2)	MRL-10x MRL <20 RPD 10x MRL-High Cal Level <10 RPD

9. Maintenance Schedule

- 9.1. On a weekly basis, or more often if necessary, the UF membrane should be changed, the water scrubber should be changed (beads changed and baked out) and the carbon dioxide scrubber should be checked and changed as needed.
- 9.2. On a bi-weekly schedule, flows should be checked through the autosampler pump tubes and through the suppressor acid and water pump tubes. The results are to be recorded in the maintenance folder on the computer desk top.
- 9.3. The remainder of the maintenance is to be performed on either a monthly, quarterly or annual basis. The annual maintenance is covered by a maintenance contract and performed as part of the annual preventive maintenance. All other maintenance is performed by the analyst. The frequency of the remaining maintenance is summarized in Table 8.

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Table 8

Maintenance	Frequency
Triple rinse MSM water reservoir and change water.	Monthly or as needed
Triple rinse MSM acid reservoir and make fresh acid.	Monthly or as needed
Triple rinse the dilution water reservoir and change water.	Monthly or as needed
Neutralize and discharge the waste.	Monthly or as needed
Triple rinse the stock eluent bottle and make fresh 72 mM eluent.	Monthly or as needed
Change the MS acid and water pump tubes.	Monthly or as needed
Replace the RP guard disk and filter.	Monthly or as needed
Triple rinse the eluent water reservoir and change water.	Monthly or as needed
Replace the 3 inline filters	Quarterly
Change the trap on top of the eluent.	Quarterly or as needed
Change the eluent aspirating filter.	Quarterly or as needed
Replace check valves.	Annually
Replace piston seals.	Annually
Replace sapphire support rings.	Annually
Replace sample waste lines.	Annually
Clean pump rollers with deionized water.	Annually

10. References

- 10.1. Determination of inorganic anions in water by ion chromatography, Method 300.1 USEPA, Revision 1.0, August 1993.
- 10.2. Metrohm MagIC Net Tutorial, May 2007.

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Appendix I
Example of Analytical Sequence Table:

Sequence No.	Sample Description	QC Requirements
1	LRB - Blank #1	All analytes below the MDL
2	LRB - Blank #2	All analytes below the MDL
3	LFB/IPC - Laboratory Fortified Blank/ Instrument Performance Check	85-115% recovery
4	LFB Dup - Laboratory Fortified Blank Duplicate	MRL-10x MRL $\pm 20\%$ 10x MRL-High Cal Level $\pm 10\%$
5	Sample #1	
6	Sample #2	
7	Sample #3	
8	Sample #4	
9	Sample #5	
10	Sample #6	
11	Sample #7	
12	Sample #7 – Laboratory Fortified Sample Matrix	75-125% recovery all analytes
13	Sample #8	
14	Sample #9	
15	Mid CCCS – Continuing Calibration Check Standard	85-115% recovery
16	Sample #10	
17	Sample #11	
18	Sample #12	
19	Sample #12 Duplicate	MRL-10x MRL $\pm 20\%$ 10x MRL-High Cal Level $\pm 10\%$
20	Sample #13	
21	Sample #14	
22	Sample #15	
23	Sample #15 – Laboratory Fortified Sample Matrix	75-125% recovery all analytes
24	Sample #16	
25	Sample #17	
26	End CCCS – Continuing Calibration Check Standard	85-115% recovery